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(21) International Application Number: PCT/EP99/05576 (22) International Filing Date: 30 July 1999 (30.07.99) (30) Priority Data: MI98A001847 5 August 1998 (05.08.98) IT (71) Applicant (for all designated States except US): ENITEC-NOLOGIE S.P.A. [IT/IT]; Via F. Maritano, 26, I-20097 San Donato Milanese (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): BELLUSSI, Giuseppe [IT/IT]; Via Scoto, 44, I-29100 Piacenza (IT). PEREGO, Carlo [IT/IT]; Via S.S. Cornelio e Cipriano, 15/E, I-20040 Carnate (IT). ZANIBELLI, Laura [IT/IT]; Via. F. Donati, 1, I-26013 Crema (IT). (74) Agents: DE GREGORI, Antonella et al.; Ing. Barzano' & Zanardo, Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CATALYST AND PROCESS FOR THE OXIDATION OF METHANE TO METHANOL		
(57) Abstract Catalytic composition, optionally supported on an inert material, characterized in that it comprises (i) oxides and/or hydroxides of a first metal (M1) and (ii) halides of a second metal (M2), wherein M1 and M2, the same or different, are selected from metals belonging to groups IIa, IIb, IVb, VIII, Ib, Va, Lanthanides, and relative mixtures. Its preparation and use in the selective transformation of methane into methanol are also described.		

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CATALYST AND PROCESS FOR THE OXIDATION OF METHANE TO METHANOL

The present invention relates to a catalytic composition, its preparation and its use in the process for transforming methane into methanol in a single step.

5 Methane is a raw material which is widely available, often however in remote places. The transportation costs are therefore very high and its compression to liquid which is easier to transport can only take place under extreme temperature and pressure conditions.

10 Consequently, owing to the high availability of natural gas and its localisation in geographically remote places, the possibility of finding a way of converting it directly in loco to products which can be transported at a lower cost, is definitely of great interest.

15 Attention is therefore directed towards hydrocarbon products with a higher molecular weight or to oxygenated products. One of these products could be methanol, which is used as both an intermediate product for chemicals and a possible energy vector.

20 The activation of methane however is not easy owing to the strong stability of the C-H bond with respect to higher hydrocarbons; processes using oxidation reactions are therefore normally adopted.

Even in well consolidated catalytic processes such
25 as steam reforming to syngas ($\text{CO} + \text{H}_2$), it is necessary

to operate under high temperature conditions ($T > 700^{\circ}\text{C}$) and to avoid the formation of the by-product CO_2 . The numerous studies being carried out (for example oxidative coupling and oxidation in homogeneous phase) have not led
5 to industrial embodiments.

Alternatively, the activation of methane takes place either by oxidation or by halogenation or a combination of the two processes (oxy-halogenation). The most favoured products in the first case are CO_x , in the second
10 case halogen-derivatives. In both cases subsequent treatment is necessary to obtain the desired products.

As far as methanol is concerned, this is industrially produced by means of two catalytic steps: the first consists in the steam reforming reaction to give syngas
15 ($\text{CO} + \text{H}_2$), the second in the actual formation reaction of methanol, after regulating the optimum CO/H_2 ratio.

As a rule methanol can be produced starting from methane by means of two types of processes: a direct process, in which the methane is transformed into methanol in a single step; an indirect process, in which the
20 reaction takes place in several steps, i.e. a first activation step of methane and one (or more) subsequent steps for the actual production of methanol.

Typical examples of direct processes are:

25 a) Casey et al. In Ind. Eng. Chem. Res. (1994) who de-

scribe a non-catalytic process at 350-550°C and at 50 bars, with a yield to methanol of 1.8%;

b) Hunter, Gesser et al. in Appl. Cat. 1990, who describe a non-catalytic process at 350°C and 30 bars with a
5 yield to methanol of 7%;

c) Hunter, Gesser et al. in Appl. cat. 1990, who describe a catalytic process with $\text{SnO}_2/\text{Cu}/\text{SiO}_2$ at 250°C and 30 bars with a yield to methanol of 3.3%;

d) Chun, Anthony in Ind. Eng. Chem. Res. (1993) who describes a non-catalytic method at 430-500°C and 50
10 bars, with a yield to methanol of less than 2%;

e) Chun, Anthony in Ind. Eng. Chem. Res. (1993) who describes a catalytic method with CuMo (or FeMo) / SiO_2 at 430-500°C and 50 bars, with a yield to methanol of
15 less than 3%.

All these direct processes have the disadvantage of not reaching yields higher than 7%.

In this respect, it should be pointed out that, although the reaction ΔG of the oxidation of methane to
20 methanol is negative, the reaction ΔG s to CO and CO_2 are much more negative. This implies the necessity of operating with limited conversions of methane to keep the selectivity high or effecting quenchings of the newly-formed products to limit their subsequent oxidation.

25 A catalytic composition has now been found, which

overcomes the drawbacks mentioned above, as it allows methane to be converted to methanol in a single step with yields even higher than 7% and with selectivities higher than 90% to methanol.

5 In accordance with this, the present invention relates to a catalytic composition, optionally supported on an inert material, characterized in that it comprises (i) oxides and/or hydroxides of a first metal (M1) and (ii) halides of a second metal (M2), wherein M1 and M2, the
10 same or different, are selected from metals belonging to groups IIa, IIb, IVb, VIII, Ib, IIb, Va, Lanthanides, and relative mixtures.

 The optional inert material supporting the catalytic composition is selected from metal oxides normally used
15 for this purpose, for example, aluminum, silicon, titanium, zirconium, cerium, lanthanum, preferably aluminum and silicon.

 In the preferred embodiment, the oxides and/or hydroxides and halides are selected from oxides, hydroxides
20 and halides of Mg, Ca, Ba, La, Ni, Cu, Zn, Bi, even more preferably, Mg, Ba, Bi, Ni.

 As far as the halides are concerned, these are preferably selected from chlorides, bromides and iodides, and are even more preferably bromides.

25 The catalytic composition of the present invention

is also characterized by a molar ratio $M1/M2 \geq 1$, preferably from 1 to 2..

The catalytic composition of the present invention can be prepared by means of various techniques known to
5 experts in the field, in particular by means of sol-gel synthesis, impregnation, physical mixing of oxides and/or hydroxides and halides.

In the case of sol-gel synthesis, the same metal halides or metal salts (for example nitrates, acetates,
10 oxalates) in the latter case in acid solution of hydrohalogen acid, can be introduced during the synthesis phase.

In particular, the sol-gel synthesis process illustrated hereunder for Silicon but applicable to any type of carrier, can be described as follows (it is assumed
15 that $M1=M2$ and that a salt of $M1$, different from the halide, soluble in alcohol, is used):

- a) a solution, normally alcohol, of a salt of the metal, is prepared;
- b) an organic source of Silicon is added to the solution of step (a);
20
- c) an aqueous solution of hydrohalogen acid is added to the solution of step (b), thus obtaining a gel;
- d) the gel of step (c) is aged at a temperature lower than 100°C , preferably at a temperature ranging from
25 10°C to 60°C ;

- e) the aged gel of step (d) is dried, preferably up to a temperature of 100°C;
- f) the gel of step (e) is calcined, preferably up to a maximum temperature of 300-500°C and even more preferably at a maximum temperature of 300-350°C, preferably in a stream of nitrogen.

It is obvious that when a metal halide is used in step (a), during step (c) it is sufficient to add water for the gelation to take place.

- Finally, when the metal salt of step (a) is insoluble in alcohol, it is dissolved in an aqueous solution, preferably acid by hydrohalogen acid, whereas the Silicon source in step (b) is put in an alcohol solution. The gelation takes place by the simple addition of the Silicon solution to the metal solution. With reference to this latter possibility, a simplified preparation scheme of the catalytic composition of the present invention can therefore be represented as follows:

Si precursor in alcohol + aqueous solution of the metal + HX --> hydrolysis --> ageing --> drying --> calcination.

When the synthesis of the supported oxides alone is effected, during step (c) an aqueous solution is added which is acid by HNO₃ or basic by the addition of an ammonium salt in relation to the precipitation pH of the

hydroxide, which produces the desired oxide during the calcination phase.

The materials thus obtained mainly consist of an amorphous carrier in which the halides and/or oxides-
5 hydroxides are uniformly dispersed.

Alternatively, the above compositions can be prepared by impregnation of the carrier with solutions of metal salts in acid solution by hydrohalogen acid, preferably selected from HBr and HCl.

10 In the case of preparation by impregnation, commercial carriers or carriers obtained by the sol-gel method, following the procedure described above, can be used.

The molar ratios used in the preparation of the catalytic composition of the present invention (again in
15 the case of the sol-gel system and assuming that $M_1=M_2$) are:

M/SiO_2 = from 0.05 to 0.40, preferably from 0.1 to 0.30;

$EtOH/SiO_2$ = from 1.8 to 4.5, preferably from 2.2 to
20 3.2;

$H_2O/EtOH$ = from 0.005 to 10, preferably from 0.01 to 4.6;

H_2O/SiO_2 = from 0.01 to 20, preferably from 0.04 to 10.5.

25 The same M/SiO_2 ratio applies when the impregnation

technique or commercial oxides are used.

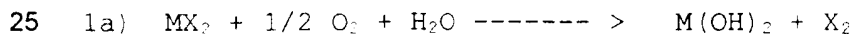
The present invention also relates to a process for the preparation of methanol starting from methane and oxygen, preferably air, under catalytic conditions, characterized in that the methanol is produced directly in the presence of the catalytic composition defined above.

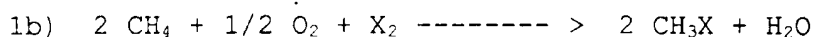
In the preferred embodiment, the process of the present invention is carried out in a continuous system, in a stream of methane and air, at pressures close to atmospheric pressure, at temperatures ranging from 250°C to 450°C, preferably from 300°C to 350°C, with a WHSV in methane ranging from 0.01 to 1 h⁻¹ and a CH₄/O₂ ratio higher than 1.8/1 or lower than 0.7/1 within the temperature range indicated, to avoid falling within explosive limits. H₂O, in vapour form, may optionally be fed, in a ratio CH₄/H₂O ranging from 0.1/1 to 3/1, preferably from 0.3 to 2.5.

Theoretical reaction schemes are provided hereunder, for the case of bivalent metals, on whose active sites the chemical species methane and oxygen are absorbed and transformed.

In these schemes M, selected from M1 and M2, represents the metal and X the halogen.

Scheme 1:

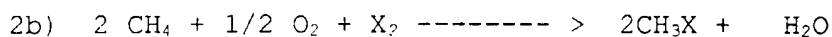




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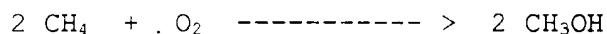


Scheme 2:

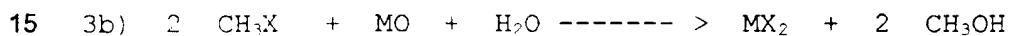
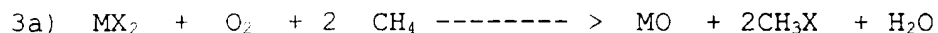


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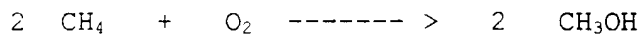
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Scheme 3:



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The process of the present invention does not comprise feeding of the halogen (or organic halides) together with the reagent mixture, as described in 2-step processes (oxyhalogenation of methane and subsequent hydrolysis).

This results in a considerable advantage for environmental impact, and in a smaller volume of reagents in

circulation. On the other hand the halides favour the activation of methane and its subsequent transformation, limiting oxidation to CO_x . In addition their effect is maintained over a period of time as they are present in
5 the catalyst.

The process of the present invention can be effected in the presence of one or more catalytic beds.

According to an embodiment of the process of the present invention, the gaseous mixture is sent to a single catalytic bed containing the catalytic composition of
10 the present invention.

According to another embodiment, the CH_4/O_2 mixture is fed to a first catalyst containing the metal halide (with the consequent activation of the methane). The mixture from this first catalyst is then fed to a second catalyst containing the metal oxide, with the consequent
15 production of methanol.

It is possible to operate in two catalytic beds at temperatures ranging from 200°C to 500°C , preferably from
20 300°C to 360°C .

According to another embodiment, the first catalytic bed is put at a temperature ranging from 300°C to 360°C , whereas the second bed is put at a temperature ranging from 70°C to 150°C .

25 Under the assumption of operating in the presence of

two catalytic beds and that the first catalytic bed has possibly been either partially or totally transformed from halide to oxide (and the second from oxide to halide), the flow of reagents or catalytic beds can be inverted.

It is essential however for the mixture of CH_4/O_2 to be fed first of all to the catalyst containing the halide and subsequently to the catalyst containing the metal oxide.

The following examples provide a better understanding of the present invention.

In these examples, the synthesis molar ratios of the catalytic systems are:

$$\text{M}/\text{SiO}_2 = 0.1 - 0.26$$

$$\text{EtOH}/\text{SiO}_2 = 2.2 - 3.2$$

$$\text{H}_2\text{O}/\text{EtOH} = 0.01 - 4.6$$

$$\text{H}_2\text{O}/\text{SiO}_2 = 0.04 - 10.5$$

EXAMPLES

Examples of the catalytic systems with NiBr_2 , MgBr_2 , BiBr_3 , NiO , $\text{Ba}(\text{OH})_2$ are provided hereunder.

In evaluating the catalytic activity of the catalysts listed above, the catalytic activity is evaluated as follows:

$$\text{Conversion: } 100 * (\text{CH}_4\text{in} - \text{CH}_4\text{out}) / (\text{CH}_4\text{in})$$

$$\text{Selectivity: } 100 * (\text{CH}_3\text{OH}/\text{Tot.products})$$

EXAMPLE 1 - Preparation of catalyst A.

3.1 grams of NiBr_2 are dispersed in 13.64 grams of EtOH under stirring at 50°C . 19.78 grams of TES (tetraethylorthosilicate) and then 8.40 grams of H_2O are added
5 to this solution. The molar ratio Ni/Si is 0.15, whereas the molar ratio Br/Ni = 2. The solution is left under stirring at 50°C until gelation (about 48 hours). This is followed by the ageing phase at room temperature for 16 hours, and then the drying phase in an oven at atmospheric pressure at 100°C for 1.5 hours. It is then calcined in muffle with the following temperature program:
10 heating in N_2 to 340°C ($5^\circ\text{C}/\text{min.}$); pause at 340°C for 3 hours; finally spontaneous cooling to room temperature.

The characteristics of catalyst A are indicated in
15 Table 1.

EXAMPLE 2 - Preparation of catalyst B

Catalyst B is prepared according to the procedure adopted in example 1 and using the same reagents as example 1 in the same molar ratio.

20 The characteristics of catalyst B are indicated in Table 1.

EXAMPLE 3 - Preparation of catalyst C

2.49 grams of $\text{MgC}_4\text{H}_{10}\text{O}_2$ (Magnesium Ethylate) are dispersed in 9.05 grams of EtOH under stirring at 50°C and
25 18.16 grams of TES followed by 20.6 grams of HBr 20% by

weight are then added.

The solution is left under stirring at 50°C until gelation (after about 53 hours). This is followed by the ageing phase at room temperature for 10 hours, and the
5 drying phase in an oven at atmospheric pressure at 100°C for 2 hours. It is then calcined in muffle with the same temperature program as example 1.

Molar ratio Mg/Si = 0.25; molar ratio Br/Mg = 2.

The characteristics of catalyst C are indicated in
10 Table 1.

EXAMPLE 4 - Preparation of catalyst D

5.869 grams of $\text{Bi}(\text{NO}_3)_3$ are dispersed in 9.14 grams of EtOH under stirring at 50°C; 15.23 grams of TES, 4.23 grams of H_2O and 17.20 grams of HBr 20% by weight are
15 added in order to this suspension. The suspension is left under stirring at 50°C until gelation (about 30 hours). The other steps are the same as those described in example 3.

Molar ratio Bi/Si = 0.20; molar ratio Br/Bi = 3.

20 The characteristics of catalyst D are indicated in Table 1.

EXAMPLE 5 - Preparation of catalyst E (NiO).

20 grams of $\text{Ni}(\text{OH})_2$ are calcined in muffle at 600°C for 5 hours in air.

25 The characteristics of catalyst E are indicated in

Table 1.

EXAMPLE 6 - Preparation of catalyst F (BaO/SiO_2).

2.32 grams of Ba(OH)_2 are dispersed in 8.99 grams of EtOH under stirring at 5°C ; 13.94 grams of TES and then
5 4.05 grams of H_2O are added to this suspension and the mixture is acidified with HNO_3 at 35%. The suspension is left under stirring at 50°C until gelation (about 70 hours). This is followed by the drying and calcination procedure described in example 3, except that the calci-
10 nation temperature is 450°C .

The characteristics of catalyst F are indicated in Table 1.

EXAMPLE 7 - Catalytic activity of the catalytic composition (A+E).

15 The catalytic system consisting of two catalytic beds, is put in a quartz reactor using corindone (40 mesh) as filler. The first catalytic bed consists of 2.2 grams of catalyst A, granulated to 30/50 mesh and diluted with 1 cc of quartz 18 mesh; the second catalytic bed
20 consists of 1.02 grams of catalyst E (30/50 mesh). Once charged into the respective reactors, catalyst A is brought to 355°C for 1 hour in a stream of N_2 (30 ml/min) whereas catalyst E is maintained at 100°C in a stream of nitrogen (30 ml/min). At these temperatures, obtained by
25 exploiting the various heated zones of the oven in which

the reactor is situated, the N_2 is closed and CH_4 and air ($CH_4/O_2 = 3$) are then fed at a $WHSV = 0.1 \text{ h}^{-1}$ (referring to the methane).

EXAMPLE 8 - Catalytic activity of the catalytic composition (C + $Ba(OH)_2$).

2.31 grams of catalyst C and 1.23 grams of $Ba(OH)_2$ are treated as in example 7, except that catalyst C is brought to a temperature of 345°C and the $Ba(OH)_2$ to 75°C .

The catalytic activity is indicated in Table 2.

EXAMPLE 9 - Catalytic activity of the catalytic composition (D + $Ba(OH)_2$).

2.20 grams of catalyst D and 1.20 grams of $Ba(OH)_2$ are treated as in example 6, except for the $WHSV = 0.05 \text{ h}^{-1}$.

The activity of this catalytic composition is illustrated in Table 2.

COMPARATIVE EXAMPLE 10 - Catalytic activity of catalyst A.

1.02 grams of catalyst A alone, granulated to 30-50 mesh, are diluted and treated as in example 7, except that the oven is heated to a single temperature of 360°C and the $WHSV$ is equal to 0.3 h^{-1} . The activity of this catalyst is indicated in Table 2.

EXAMPLE 11 - Catalytic activity of the catalytic composition

tion (C + Ba(OH)₂).

2.31 grams of catalyst C and 1.23 grams of Ba(OH)₂ are mechanically mixed, granulated to 30-50 mesh and diluted as in example 7, except that the catalytic system
5 obtained by mixing is brought to a single temperature of 300°C and WHSV = 0.05 h⁻¹.

The activity of this catalytic composition is indicated in Table 2.

EXAMPLE 12 - Catalytic activity of the catalytic composition (C + F)
10

2.11 grams of catalyst C and 1.16 grams of catalyst F are mechanically mixed, granulated to 30-50 mesh, diluted as in example 7, except that the catalytic system obtained by mixing is brought to a single temperature of
15 300°C and WHSV = 0.06 h⁻¹. H₂O is then fed by means of a double piston pump at a flow-rate equal to 0.001 ml/h, sent to a preheater brought to 200°C where it is mixed in the form of vapour with the reagent gases before being sent to the reactor.

20 The activity of this catalytic composition is indicated in Table 2.

TABLE 1

		Cat A	Cat B	Cat C	Cat D	Cat E	Cat F
5	Surf.area	490	450	340	90	90	20
	M/SiO ₂	0.11	0.15	0.25	0.2	---	0.2
	Br/M	2	2	2	3	---	---
10	M	Ni	Ni	Mg	Bi	Ni	Ba

TABLE 2

15	Example	7	8	9	10c	11	12
	Catal.	A+E	C+Ba(OH) ₂	D+Ba(OH) ₂	A	C+Ba(OH) ₂	C+F
20	Conv.CH ₄	2.24	2.2	9	4	5.3	9.9
	Sel.CH ₃ OH	100	99.7	100	20	100	100
	Sel.CH ₃ Br	---	0.3	---	80	---	---
25							

The results of Table 2 demonstrate the capacity of the various catalytic systems of effecting the activation of methane under bland temperature conditions, with low conversions to methane but accompanied by almost total selectivity to methanol, especially in the case of the coupling of several catalytic systems, in particular the system $\text{BiBr}_3/\text{SiO}_2$ and $\text{Ba}(\text{OH})_2$ (example 9) and Mg/Ba (example 12).

CLAIMS

1. A catalytic composition, optionally supported on an inert material, characterized in that it comprises (i) oxides and/or hydroxides of a first metal (M1) and (ii) halides of a second metal (M2), wherein M1 and M2, the same or different, are selected from metals belonging to groups IIa, IIb, IVb, VIII, Ib, IIb, Va, Lanthanides, and relative mixtures.
2. The catalytic composition according to claim 1, wherein the inert material is selected from the oxides of aluminum, silicon, titanium, zirconium, cerium, lanthanum.
3. The catalytic composition according to claim 2, characterized in that the inert material is selected from the oxides of aluminum and silicon.
4. The catalytic composition according to claim 1, characterized in that M1 and M2, the same or different, are selected from Mg, Ca, Ba, La, Ni, Cu, Zn, Bi.
5. The catalytic composition according to claim 4, wherein M1 and M2, the same or different, are selected from Mg, Ba, Bi, Ni.
6. The composition according to claim 1, characterized in that the halides are selected from chlorides, bromides and iodides, and are preferably bromides.

7. The catalytic composition according to claim 1, wherein the molar ratio $M1/M2 \geq 1$, is preferably from 1 to 2.
8. A process for the preparation of the catalytic composition according to claim 1, said process being selected from sol-gel synthesis, impregnation, physical mixing of oxides and/or hydroxides and halides.
9. A process for the preparation of methanol starting from methane and oxygen, preferably air, under catalytic conditions, characterized in that the methanol is produced directly in the presence of the catalytic composition according to claim 1.
10. The process according to claim 9, characterized in that the preparation of methanol is carried out in a system in continuous, in a stream of methane and air, at pressures close to atmospheric pressure.
11. The process according to claim 10, characterized in that the temperature ranges from 250°C to 450°C, the molar ratio CH_4/O_2 is higher than 1.8/1 or less than 0.7/1 within the above temperature range, optionally in the presence of vapour, the molar ratio CH_4/H_2O being from 0.1/1 to 3/1.
12. The process according to claim 11, characterized in that the temperature ranges from 300°C to 350°C and

the molar ratio $\text{CH}_4/\text{H}_2\text{O}$ ranges from 0.3/1 to 2.5/1.

13. The process according to claim 10, characterized in that the mixture CH_4/O_2 is sent to a first catalytic bed, essentially containing the metal halide (i),
- 5 the mixture leaving the first catalytic bed subsequently being sent to a second catalytic bed essentially containing the oxide (ii).
14. The process according to claim 13, characterized in that the temperature of both catalytic beds ranges
- 10 from 200°C to 500°C, preferably from 300°C to 360°C.
15. The process according to claim 13, characterized in that the temperature of the first catalytic bed ranges from 300°C to 360°C, whereas the temperature of the second catalytic bed ranges from 70°C to
- 15 150°C.
16. The process according to claim 13, characterized in that the flow of reagents or catalytic beds can be inverted.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/05576

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J27/08 B01J23/02 C07C29/50 C07C31/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB 1 244 001 A (ICI LTD.) 25 August 1971 (1971-08-25) page 1, line 42 - line 50 ---	9-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

29 November 1999

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/05576

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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